

Stress Relaxation of Oriented Nylon 6 Fibers

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Synopsis

The stress relaxation of oriented and dried nylon 6 fibers was measured at temperatures ranging from room temperature to 423 K using a simple tensile method. After the reduction for temperature and crystallinity by Nagamatsu et al.'s procedure,² the relaxation modulus curves were shifted along a time axis, and master curves were obtained. The Arrhenius plots of shift factor was represented by two straight lines having a break point, the temperature of which was in approximate agreement with those of the breakdown of hydrogen bonds in the amorphous region. The relationship between the breakdown of hydrogen bonds and the values of apparent activation energies for relaxation is discussed. It was found that the effects of hydrogen bonds on the relaxation behavior are similar to those of crosslinking points in crosslinked polymers. Moreover, from the constants C_1 and C_2 of the WLF equation, the free volume fraction at $T_g(f_g)$ and the expansion coefficient of free volume at $T_g(\alpha_f)$ were estimated to be 0.013 and 4.2×10^{-5} , respectively. Finally, through the use of the usual primary approximation method, the relaxation time spectra were obtained from the relaxation master curves. The obtained spectra showed two distributions of wedge type and box type. When the draw ratio increases, the height of distribution of the box type becomes higher and its position shifts to a longer time side, whereas those of the wedge type remain virtually unchanged.

INTRODUCTION

The stress relaxation for crystalline polymers has been reported.¹⁻⁶ However, the theoretical and phenomenological analyses for the relaxation processes have not been performed sufficiently, due to the effect of crystallites on the relaxation of molecular segments in the amorphous region. For a more detailed analysis, it is necessary to detect even slight changes in the relaxation behavior with respect to time, temperature, and frequency.

In the present study, the measurements of stress relaxation have been carried out by a simple tensile method using a high-sensitivity strain gauge on oriented and dried nylon 6 fibers over a wide temperature range from room temperature to 423 K. This is far higher than the highest measuring temperature,⁶ 354 K, in previous studies for nylon 6. Consequently, it has been found that some relaxation properties, such as the features of master relaxation curves and of relaxation time spectra and the temperature dependence of shift factor, differ from those in the previous studies.³⁻⁶

The purpose of the present paper is to present these experimental results and discuss the effects of crystallites and hydrogen bonds on the relaxation behavior as compared with those of crosslinking sites in crosslinked polymers.

EXPERIMENTAL

Material

The material used in the present study is nylon 6 fiber (819.6 den/15 filaments) supplied by Toyo Rayon Co. Ltd. It has an average molecular weight of ca. 18,000. Before the measurements of stress relaxation, the original fibers were drawn up to threefold or fourfold under conditions of 23–25°C and ca. 65% R.H., and were then dried in a desiccator over phosphoric acid anhydride for two months (Table I). The degrees of crystallinity and the orientation factors of crystalline region (f_c) were determined by x-ray diffraction,⁷⁻⁹ the total birefringences were measured by the Berek compensator method,^{7,8} and the orientation factors of amorphous region (f_a) were calculated.⁹

Measurements

A tension tensile tester was used to measure the relaxation moduli: Tensilon UTM-II, SS-105-UTM (Toyo-Baldwin Co. Ltd.) equipped with an electric furnace which could be kept at a desired temperature by an automatic system. The dimensions of the specimens are 50 mm in length and ca. 2×10^{-3} mm² in cross section.

The specimens were heated to a desired temperature for 5 min at a heating rate of 4°C/min under a tensionless state in a dry nitrogen gas stream. Then, a small strain, which had been previously ascertained to satisfy a linearity of viscoelasticity, was imposed upon the specimens. This strain is 1% in reference to the length of the drawn specimen at this temperature. The relaxation moduli were measured at various temperatures between room temperature and 423 K for 100 min in a dry nitrogen gas stream. The different specimens, which were prepared under the same conditions, were used separately at varying temperatures since the degrees of crystallinity varied according to the temperature.

RESULTS AND DISCUSSION

The viscoelastic properties of a hydrophilic polymer are very sensitive to the absorbed moisture or relative humidity. Therefore, in order to avoid the complex effects of moisture on relaxation behavior, we measured the relaxation moduli under moisture-free conditions on the dried specimens drawn up to threefold and fourfold, as described above. The obtained relaxation moduli were reduced according to Nagamatsu et al.'s procedure² which is expressed by the following equation:

$$\log E_r(t)_{\text{red}} = \log E_r(t) + \log \frac{T_0}{T} - \log \frac{\Lambda}{1 - \Lambda} + \log \frac{\Lambda_0}{1 - \Lambda_0} \quad (1)$$

TABLE I
Characteristics (at 293 K) of the Specimens Used for Measurement of Relaxation Modulus

Specimen	Crystallinity, %	Birefringence ($\times 10^8$)	f_c	f_a
Drawn up to threefold	45.2	40.66	0.756	0.374
Drawn up to fourfold	46.4	50.30	0.783	0.598

where $E_r(t)_{\text{red}}$ is the reduced relaxation modulus, $E_r(t)$ is the relaxation modulus as measured, T is the measuring temperature, T_0 is the reference temperature (the glass transition temperature of nylon 6, 323 K¹⁰), and Λ_0 and Λ are the crystallinities at T_0 and T , respectively. The curves of $\log E_r(t)_{\text{red}}$ versus $\log t$ for the specimen drawn up to fourfold are shown in Figure 1. On the other hand, the degree of crystallinity decreased from 45.2% to 38.8% for the threefold drawn specimen and from 46.4% to 39.2% for the fourfold one over a temperature range from 293 to 473 K (Fig. 2). The value of crystallinity at each temperature was used in the calculation of eq. (1). The variations in crystallinity with time at certain temperatures were also checked by x-ray diffraction and were found to be negligibly small; namely, the degree of crystallinity remained virtually unchanged throughout the measurement of the relaxation modulus at a constant temperature.

Assuming that the principle of time-temperature superposition is applicable to nylon 6, we prepared master curves for relaxation moduli. Consequently, the master curves, shown in Figure 3, were easily obtained by shifting the reduced

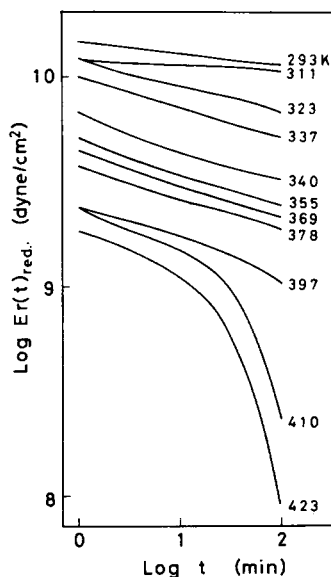


Fig. 1. Time dependence of relaxation modulus $E_r(t)_{\text{red}}$ at various temperatures for nylon 6 fiber drawn up to fourfold. The data are reduced according to the procedure of Nagamatsu et al.

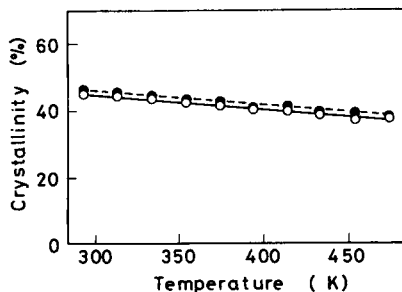


Fig. 2. Change in crystallinity of oriented nylon 6 fibers with temperature: (O) specimen drawn up to threefold; (●) specimen drawn up to fourfold.

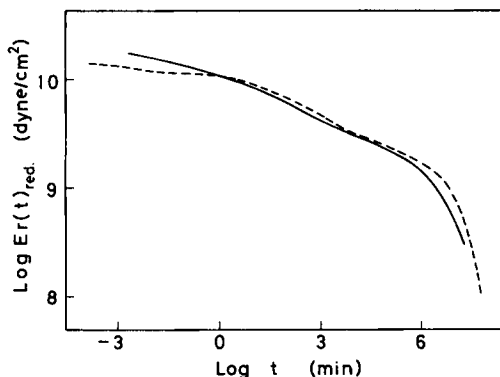


Fig. 3. Master curves of relaxation modulus $E_r(t)_{red}$ for oriented nylon 6 fibers: solid line, specimen drawn up to threefold; broken line, specimen drawn up to fourfold. The reference temperature is 323 K for both specimens.

relaxation curves only along the time axis. In this case, the curve at 323 K was used as a reference curve. A fluid region can clearly be seen on the long-time side in each case of specimens drawn up to three- and fourfold (Fig. 3).

Moreover, Figures 4 and 5, respectively, show the relations between temperature T and logarithm of shift factor, $\log a_T$, and between the reciprocal of the temperature $1/T$ and $\log a_T$. Each curve of $\log a_T$ versus $1/T$ can be represented by two straight lines intersecting at one point (Fig. 5). This fact indicates that there are two relaxation mechanisms with different apparent activation energies in the temperature ranges below and above the break point. The temperatures of these break points agreed approximately with those¹¹ (350–385 K) of the α -transition caused by the breakdown of hydrogen bonds in the amorphous region.

Similar relations between $\log a_T$ and $1/T$, which are composed of two straight lines, have also been reported for nylon 6 by Hoashi and Andrews,¹² for polyethylene by Takayanagi,¹³ and for unsaturated polyester by Kitoh et al.¹⁴ Data according to Hoashi and Andrews were obtained from a measurement of dynamic viscoelastic property (Fig. 5). In spite of the difference between the experimental methods, the Arrhenius plot features certain similarities to those obtained by the authors. Recently, it has also been found by Kodama¹⁵ that the relationship between $\log a_T$ and $1/T$ for a reinforced epoxy resin is represented by three straight lines; the three values of ΔH_a calculated from each line become smaller, in the order of lower, medium, and higher temperature ranges.

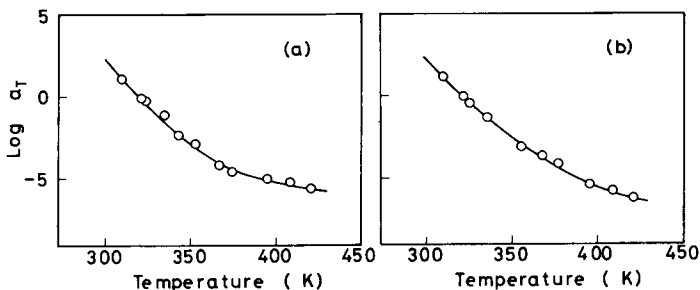


Fig. 4. Temperature dependence of logarithm of shift factor for oriented nylon 6 fibers: (a) specimen drawn up to threefold; (b) specimen drawn up to fourfold.

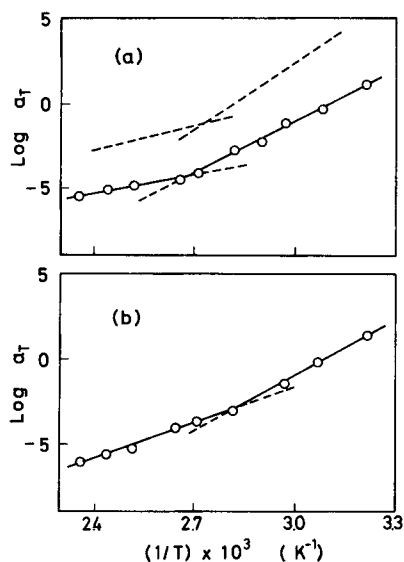


Fig. 5. Plots of logarithm of shift factor against reciprocal of absolute temperature for oriented nylon 6 fibers: (a) specimen drawn up to threefold; (b) specimen drawn up to fourfold. Broken line shows the data by Hoashi and Andrews.¹²

The values of the apparent activation energy for relaxation (ΔH_a) are summarized in Table II together with the temperatures of the break points. The values of ΔH_a were calculated from the slope of each straight line in Figure 5 by eq. (2):

$$\Delta H_a = R d \ln a_T / d(1/T) \quad (2)$$

where R is the gas constant. The value of ΔH_a in high-temperature ranges above the break point is smaller than that in low-temperature ranges below the point (Table II). Hence, a value of ΔH_a for relaxation is regarded as a measure of the difficulty of movement of molecular segments. Namely, when the hydrogen bonds are broken down at a temperature near the break point, the mobility of segments increases and the values of ΔH_a , consequently, decrease. Furthermore, the value of ΔH_a for the specimen drawn up to fourfold is larger than that for the specimen drawn up to threefold in the temperature range above the break point. When the orientation and crystallinity increase by elongation, the motion of molecular segments in the amorphous region must be inhibited.

TABLE II
Apparent Activation Energies (ΔH_a) and Temperature of the Break Points in Arrhenius Plots

Specimen	ΔH_a , kcal/mole	Temp. of break point in Arrhenius plot, K
Drawn up to threefold	17 (high temp.)	371
	47 (low temp.)	
Drawn up to fourfold	33 (high temp.)	350
	49 (low temp.)	
Data by Hoashi and Andrews ¹² (annealed at 433 K)	34 (high temp.)	380
	60 (low temp.)	

On the other hand, Kitoh et al.¹⁶ and Shibayama et al.¹⁷ reported for unsaturated polyester and crosslinked epoxy resin, respectively, that the values of ΔH_a for relaxation increase with an increase in the crosslinking density in temperature ranges above T_g . If the hydrogen bonds in nylon 6 would act as crosslinking sites in crosslinked polymers, a similar interpretation^{16,17} could be offered for the difference between two values of ΔH_a in the temperature ranges above and below the break point.

Williams, Landel and Ferry¹⁸ introduced a relationship between a_T and temperature T for almost nonpolar amorphous polymers:

$$\log a_T = -C_1(T - T_g)/(C_2 + T - T_g) \quad (3)$$

where T_g is the glass transition temperature and C_1 and C_2 are constants. In order to check the applicability of this equation to semicrystalline nylon 6, the relation between $(T - T_g)/\log a_T$ and $T - T_g$ in the following equation, derived from eq. (3), was plotted:

$$\frac{T - T_g}{\log a_T} = -\frac{C_2}{C_1} - \frac{T - T_g}{C_1} \quad (4)$$

The obtained curves were also composed of two straight lines, (Fig. 6). From the slope and the intercept of the straight line in the lower-temperature range including T_g , C_1 , and C_2 for the specimen drawn up to threefold were determined to be 33 and 311, respectively. The values of C_1 and C_2 obtained for the specimen drawn up to fourfold are nearly equal to the above values, 33 and 311.

C_1 and C_2 can be related to the free volume fraction at T_g (f_g) and the expansion coefficient of free volume at T_g (α_f) by means of eqs. (5) and (6)

$$C_1 = B/2.303f_g \quad (5)$$

$$C_2 = f_g/\alpha_f \quad (6)$$

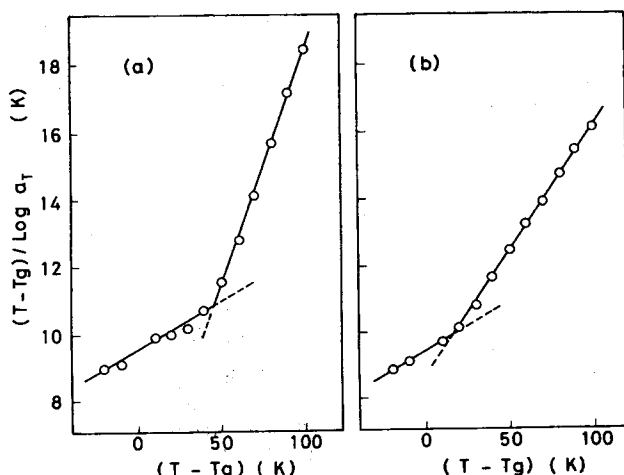


Fig. 6. Relation between $(T - T_g)/\log a_T$ and $T - T_g$ for oriented nylon 6 fibers: (a) specimen drawn up to threefold; (b) specimen drawn up to fourfold.

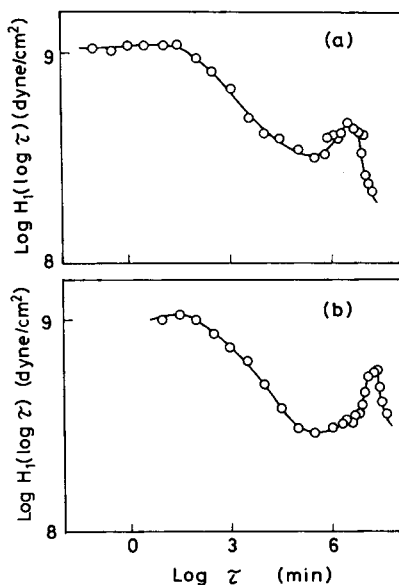


Fig. 7. Relaxation time spectra for oriented nylon 6 fibers. (a) specimen drawn up to threefold; (b) specimen drawn up to fourfold.

where B is a constant and taken as unity. By the use of eqs. (5) and (6), f_g and α_f were calculated to be 1.3×10^{-2} and 4.2×10^{-5} , respectively.

In Table III, the values of C_1 , C_2 , f_g , and α_f are compared with those for typical amorphous polymers and poly(ethylene terephthalate). The values of f_g and α_f for nylon 6 are smaller than those for amorphous polymers. However, the value of f_g , being one half of 0.025 for amorphous polymer, was in good agreement with the one for poly(ethylene terephthalate). This was calculated from Thompson and Woods' data²⁰ by Takayanagi et al.,²¹ who found this value as reasonable as f_g for a partial crystalline polymer having a crystallinity of 48%. On the other hand, Shibayama et al.¹⁷ and Kitoh et al.²² reported that the values of f_g and α_f for unsaturated polyester and for epoxy resin, respectively, decrease regularly with increase in the crosslinking density. Now, it is possible to assume that the effect of crystallites in crystalline polymers on f_g and α_f is similar to that of crosslinking points in crosslinked polymers. The crystallites, as well as the crosslinking sites, seem to prevent the segmental motion of amorphous chains and to restrict the thermal expansion of free volume. In the case of nylon 6, compared with poly(ethylene terephthalate), the effect of the hydrogen bonds must overlap on that of the crystallites.

The relaxation time spectra, finally, were determined from the master curves of $E_r(t)_{\text{red}}$ by the use of the usual primary approximation method:

TABLE III
Values of C_1 , C_2 , f_g , and α_f for Drawn Nylon 6 Fiber, Unoriented Poly(ethylene Terephthalate) Fiber,^a and Amorphous Polymer

Polymer	C_1	C_2	f_g	α_f , deg ⁻¹
Drawn nylon 6 fiber	32.9	311.3	0.013	4.2×10^{-5}
Unoriented poly(ethylene terephthalate) fiber	31.25	109.3	0.014	1.27×10^{-4}
Amorphous polymer	17.44	51.6	0.025	4.8×10^{-4}

^a From Takayanagi et al.²¹

$$H_1(\log \tau) = -E_r(t)_{\text{red}} \frac{d \log E_r(t)_{\text{red}}}{d \log t} \quad (7)$$

The obtained spectra are shown in Figure 7. The relaxation spectra of textile fibers can be approximated⁴ well only by box-type distribution; the spectra obtained here have clearly shown both wedge-type and box-type distributions, similar to those of typical amorphous polymers. The wedge-type distribution, however, is flatter and higher than those of amorphous polymers; the slopes are about $-1/5$ and are significantly smaller than the theoretical slope of $-1/2$, according to Rouse.²³ When the draw ratio increases from threefold to fourfold, the box-type distribution becomes higher and its position shifts to the longer-time side, whereas the wedge type remains almost unchanged. Thus, the box-type distribution is influenced by an increase in orientation and crystallinity caused by elongation. Additional experiments are planned to clarify the relationship of the box-type distribution to the structural changes in the crystalline region.

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